Letters to the Editor

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Intramolecular group rotation and hindrances in O-amino phenol : A PMR study

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Proton Magnetic Resonance studies were undertaken within the temperature range of 77°K to 423°K. The sample of *O*-amino phenol was obtained from B.D.H. (India). Molecules of *O*-amino phenol were taken to be planar. Existence of hydrogen bond from O to O was expected. But Hans *et al* (1964) could not confirm the existence of hydrogen bonding by their infrared studies. In the present study an attempt has been made to picturise the rotation of groups in the presence of steric and other hindrances. The experiment was performed at Tata Institute of Fundamental Research, Bombay on the Varian V-4340 assembly. Results were arrived at by comparing the experimental second moment with the theoretical second moment.

The second moment S consists of (i) Intramolecular contribution (S_1) and (ii) Intermolecular contributions (S_2). S_1 has been calculated by constructing a molecular model using the structural parameters given by Kitaigorodski (1948), the C–N, N–H bond lengths and $<$ HNH was taken from the tables of interatomic distances. Using Van Vleck's (1948) expression, S_1 was found to be 8·98 gauss^2. S_2 was calculated from the simplified expression of Smith (1965) i.e., $S_2 = 358{\cdot}1 \times 4\pi\ N_p(3R^3V)^{-1}$, where $N_p = 28$, $R = 2{\cdot}48$Å, $V = 614{\cdot}62$Å, S_2 was found to be 4.47 gauss^2. Thus the total theoretical rigid lattice second moment comes out to be 13·45 gauss^2. The probable error in the determination of S is $\pm$ ·9 gauss^2. Second moment versus temperature curve is shown in figure 1.

The fall in S after 364°K led us to explore the possibility of intramolecular group rotation. Mehrotra *et al* (1967), Morozova *et al* (1968), found that dielectric relaxation time was high for *O*-amino phenol than for para or meta amminophenol; thus was interpreted as due to the presence of hydrogen bonding and steric hindrances in *O*-amino phenol acting as a potential barrier to the intra molecular group rotation.

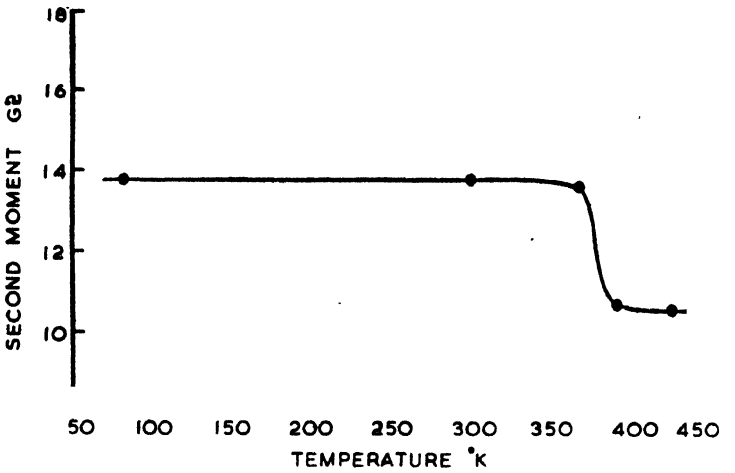

Fig. 1. Variation with temperature of the second moment of the absorptoion line in O-aminophenol.

Batterhan (1964) has shown that a substitution at the ortho position leads to an increased interaction. To examine this interaction, we take cognizance of the fact that there are two possibilities of group rotation (i) NH_2-group rotation and (ii) OH-group rotation. The decrement in the value of the second moment for NH_2-group reorientation comes out to be 3·28 gauss^2 (Agarwal 1972) and the reduction in case of OH-group rotation is in the range 4·58 to 5·25 gauss^2. This was for the rotation of the groups independently. Using the reduction factors given by Smith (1965) the reduction in the second moment for the simultaneous reduction of the two groups is found to be in the range 6·74 gauss^2 to 7·50 gauss^2. Since the observed reduction in the experimental value of the second moment is 3·12 gauss^2, we believe that the line-width reduction is due to the rotation of NH_2-group only. We differ from the conclusion drawn by Mehrotra *et al* (1967) that a restricted motion of both the groups takes place in this compound and we feel the strong H-bonding prevents hydroxyl group rotation and only amino group motion takes place.

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